

Comparison of gas temperatures measured by coherent anti-Stokes Raman spectroscopy (CARS) of O₂ and N₂

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We investigate the accuracy of temperature measurements by coherent anti-Stokes Raman spectroscopy (CARS) of O₂ and use measurements taken with N₂ CARS and a thermocouple for comparison. Scanning vibrational CARS spectra of O₂ and N₂ were recorded over a broad range of temperatures: between 294 K and 1900 K in air that was heated in a tube furnace and at approximately 2450 K in a fuel-lean CH₄-O₂-N₂ flame. Temperatures were derived from least-squares fits of simulated and experimental spectra. Both the fundamental vibrational band and the first hot vibrational band were included in fitting. In the case of the tube furnace, the N₂ and the O₂ CARS temperature measurements agreed to within 3%, and results were similar with the thermocouple; in the flame the agreement was to within 1%. We conclude that, for cases in which O₂ is present in sufficient concentrations ($\approx 10\%$ or greater), the accuracy of O₂ thermometry is comparable with that of N₂. © 2001 Optical Society of America
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1. Introduction

Coherent anti-Stokes Raman spectroscopy (CARS) of N₂ is a widely accepted standard for thermometry in combustion environments because N₂ is present in high concentrations in nearly all regions of air-fed combustion systems; consequently, CARS of N₂ has received considerable development.¹ However, for applications that require higher gas temperatures, higher heat transfer, reduction of NO_x, or all three, both O₂-enhanced and oxygen-fuel combustion processes in which N₂ is not present in significant quantities are being adopted.² Thus a need exists to develop CARS thermometry further by use of major combustion species other than N₂. In particular, O₂, when present in significant quantities in fuel-lean oxygen-fuel combustors, is attractive as a probe molecule. O₂ has a relatively simple vibrational Raman spectrum with well-known spectral parameters.

In this paper, we compare the accuracy of O₂ CARS

thermometry with that of N₂. We acquire vibrational CARS spectra of O₂ and N₂ with a scanning, narrow-band dye laser and derive temperatures from least-squares fits of the experimental spectra. The resulting temperatures are compared for both molecular probes and with thermocouple measurements (at less than 1900 K) for gas temperatures ranging from 294 to 2450 K.

From motivation by the utility of N₂ CARS for thermometry of air-fed flows, the spectroscopic constants of N₂ have been accurately determined,³⁻⁴ and the collisional parameters of N₂ have been studied extensively.⁵⁻¹² O₂ CARS has been used less frequently and is more often used for concentration rather than temperature measurements. Such measurements often probe the rotational Raman transitions within the vibrational ground state, a technique referred to as pure rotational CARS. Thumann *et al.*¹³ used pure rotational CARS for the simultaneous measurement of relative N₂-O₂ concentration measurements in air. Bengtsson *et al.*¹⁴ combined rotational CARS of N₂ and O₂ with vibrational CARS of the C-H stretch resonances in hydrocarbons for simultaneous measurements of the temperature and the concentrations of fuel, O₂, and N₂. The temperature was derived from rotational CARS spectra of N₂. Martinsson *et al.*¹⁵ measured the O₂ concentration and temperature in N₂-O₂ mixtures between 290 and 1410 K with rotational CARS.

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At temperatures higher than 1000 K the relative rotational populations of the ground-state vibrational level of O₂ are not strong functions of temperature. Martinsson *et al.*¹⁵ noted that the temperature sensitivity of rotational CARS is considerably less than that of vibrational CARS, which accesses transitions between different rotational–vibrational energy levels. Hancock *et al.*¹⁶ used dual-pump vibrational CARS spectra of N₂ and O₂ to measure the O₂ concentration and temperatures to as high as 2100 K in a jet-diffusion flame.

Dreier *et al.*¹⁷ derived temperatures from vibrational CARS spectra of N₂ and O₂ in a high-temperature furnace operated to as high as 2000 K. The spectral constants for O₂ that were available to Dreier *et al.* at the time were not sufficiently accurate to simulate the spectra of the excited vibrational states, so only the fundamental ($v = 0 \rightarrow 1$) band was used in fitting. Differences between the CARS temperature measurements and the corrected thermocouple measurements were ≤ 40 K for N₂ and ≤ 80 K for O₂. The exclusion of O₂ hot bands in this study¹⁷ was later addressed by Dreier and Schiff,¹⁸ who used the recently reported O₂ spectral constants of Rouillé *et al.*¹⁹ and the collisional broadening parameters of Millot *et al.*²⁰ to fit a broadband O₂ CARS spectrum that was acquired in a furnace. The measured temperature was 1850 K with a thermocouple temperature of 1910 K. Since then, to our knowledge, little has been reported on the accuracy of thermometry by O₂ vibrational CARS. In particular, no studies have been performed for a range of temperatures or at the higher temperatures encountered in oxygen–fuel combustors.

We report an investigation of the accuracy and the precision of O₂ CARS thermometry for temperatures between 294 and 2450 K. The spectral constants of Rouillé *et al.*¹⁹ and the collisional broadening parameters of Millot *et al.*²⁰ and Fanjoux *et al.*²¹ were used to model scanned O₂ vibrational CARS spectra that were acquired with a narrow-band dye laser. Measurements were performed in a laboratory flame and in air heated in a tube furnace. Temperatures from least-squares fits of O₂ CARS spectra were compared with temperatures that were similarly determined from N₂ CARS spectra and with thermocouple measurements. The effects of including or omitting vibrational hot bands in the spectral fits was investigated. We describe the collisional and the spectral models that were found to simulate successfully the O₂ CARS spectra at different temperatures.

2. Experimental Apparatus

The experiment used a conventional three-dimensional folded BOXCAR geometry for phase matching.²² The 532-nm frequency-doubled output of an in-house-built 20-Hz Nd:YAG laser (330 mJ/pulse at 532 nm) provided the two CARS pump beams and pumped a Lambda Physik Model FL 2002 dye laser for the Stokes beam. More than 60% of the Nd:YAG output was discarded to avoid inducing Stark broadening and saturation by stimulated Ra-

man scattering. Approximately 8% of the output was used to pump the dye laser, and the remaining 30% was used for the two pump beams. The intensities of both pump beams were reduced by use of a $\lambda/2$ plate and a thin-film polarizer prior to splitting the beams. The laser dye was Kiton Red for the N₂ CARS measurements, whereas the O₂ CARS measurements used a mixture of Rhodamine 610 and Rhodamine 590 dyes. The final amplifier stage of the dye laser was not used.

The two pump beams were directed into a 750-mm focal-length focusing lens by use of a 90° turning mirror; the mirror had a 6-mm-diameter centered hole for passage of the Stokes beam. The three focused beams crossed in the measurement location. The pump beams had a beam waist of 105 μm , whereas the probe beam had a 215- μm waist. For both the room-temperature air and the furnace measurements the diagnostic volume in which more than 99% of the CARS signal was generated was measured to be 40 mm long. Because the temperature profile of the flame was not uniform over this length, the length of the diagnostic volume was reduced to 15 mm for the flame measurements. To ensure that we probed the highest-temperature flame gases for both the N₂ and the O₂ measurements, we optimized the beam alignment, while monitoring the signal with the Stokes beam tuned to a line in the first hot band.

The high-temperature furnace (CM Associates, Model 1700) was heated by eight tungsten elements. The elements were mounted in an insulated box with 78-mm-diameter circular openings into which we inserted a 76-mm outer-diameter, 70-mm inner-diameter, open-ended ceramic tube. A series of 12-mm-thick circular alumina baffles were added inside the tube to reduce temperature gradients in the probe volume. Each baffle had a centered 19-mm-diameter hole for optical access. The enclosed and insulated central region of this tube provided an excellent environment for thermocouple measurements because radiation losses from the thermocouple junction are negligible. Before performing CARS temperature measurements in the furnace, we measured axial temperature profiles at the center of the tube by using a thermocouple.

Figure 1 displays temperature measurements that were taken with a type R thermocouple (Pt 87% and Rh 13%) over the axial length of the tube. Near the center the temperature is observed to vary by only 3 K over an axial distance of 10 cm. The central heated zone is thus well suited to a comparison of N₂ and O₂ CARS measurements for which the interaction of the beams was 40 mm in length.

The CARS signal beam was sent to a Spex Model 1680 double spectrometer and detected with a Hamamatsu Model R955 photomultiplier tube. The photomultiplier tube's socket was specially wired to use only five dynodes, biased by -600 V, to avoid photocurrent nonlinearity. Portions of the 532-nm beam and the Stokes beam were split off with beam splitters and sent to Molectron Model J3-05 joulemeters to measure the pulse energies. The CARS sig-

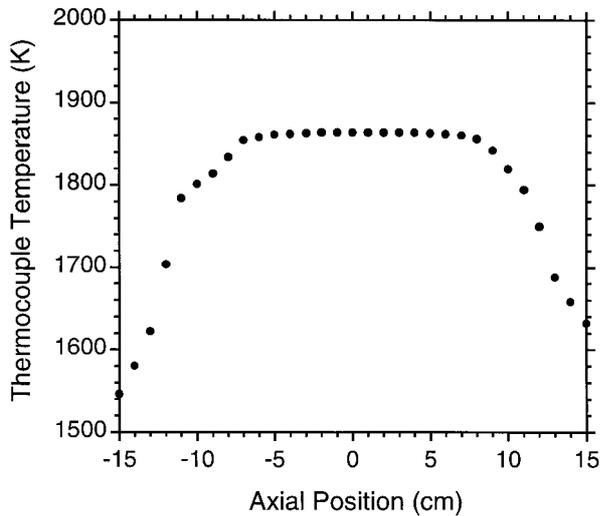


Fig. 1. Thermocouple measurements taken along the axis of the tube furnace.

nal was normalized to the Stokes pulse energy and the square of the pump-pulse energy for each individual laser shot. Special attention was given to minimizing the Stokes laser linewidth to improve the CARS spectral resolution. The spectral characteristics of the Stokes beam were monitored by the measurement of the transmission of the beam through an etalon (30-GHz free spectral range) with a linear array and a photodiode. The transmission at the center of the fringe pattern was monitored with the photodiode, whereas the outermost etalon fringes were reflected onto the linear array and displayed on an oscilloscope for monitoring the laser linewidth and the laser-amplified spontaneous emission during laser alignment.

A polarization-subtraction technique²³ was used to eliminate the nonresonant contribution to the spectra. The Stokes beam polarization was rotated by -60° with respect to the vertical pump beams, and a polarizer was placed in the path of the signal beam at $+60^\circ$ with respect to the vertical. Although this polarization scheme effectively eliminates the nonresonant background and reduces the baseline on the spectra, it also reduces the total signal strength by more than an order of magnitude. The signal also scales with the square of the interaction length, and the CARS signal was thus substantially reduced when we decreased the length of the probe volume for the flame measurements. To help offset the signal loss from the reduced interaction length, we used vertical polarizations for all the input beams and the signal polarizer.

3. Interpretation of Coherent Anti-Stokes Raman Spectroscopy Spectra

As was mentioned in Section 2, a photodiode monitored the transmission of the laser intensity through an etalon to track the linearity of the scan. Knowing the free spectral range of the etalon, we were able to account for nonlinearities in the scanning rate of the

dye laser by using the computed centroids of the etalon's transmission peaks as frequency markers. The horizontal offset of each spectrum was allowed to shift for best agreement with the line positions determined from the CARS fitting code. The spectral constants for the N_2 CARS data were taken from Gilson *et al.*,³ whereas the spectral constants for the O_2 CARS data were taken from Rouillé *et al.*¹⁹ The expression for the vibrational energy was expanded in terms of the Dunham coefficients ω_e , $\omega_e x_e$, and $\omega_e y_e$ and equated to the vibrational-energy expression of Rouillé *et al.*¹⁹ The resulting values of ω_e , $\omega_e x_e$, and $\omega_e y_e$ were 1580.0879, 11.89853, and 0.03049 cm^{-1} , respectively.

The collisional line-broadening parameters used to analyze the N_2 spectra both in room-temperature air and in the furnace were taken from the modified exponential-gap model of Farrow *et al.*²⁴ The broadening of N_2 by O_2 was considered to be identical to that of N_2 self-broadening. For temperature measurements in the flame the broadening parameters of Bonamy *et al.*¹⁰ were used to account for the different broadening effects of N_2 , CO_2 , and H_2O in the post-flame gases. For all the O_2 temperature measurements the broadening parameters were taken from Millot *et al.*²⁰ and Fanjoux *et al.*²¹ Depending on the pressure and the temperature of the probed environment, the CARS line shape can be a complex function of the collisional environment.²⁵ At low temperatures the off-diagonal elements of the relaxation matrix result in a line shape that depends on the state-to-state relaxation rates. For both room temperature and 520 K the relaxation matrix was inverted⁵ to account for the collisional narrowing in the CARS spectrum. At higher temperatures, the collision widths narrow, and the off-diagonal elements of the relaxation matrix become less important. For temperatures higher than 520 K, we assumed an isolated-line model for the CARS line broadening that ignores the off-diagonal matrix elements. For 1860 K and higher, we included the Doppler effect when calculating line shapes and assumed the CARS line shapes could adequately be described by the Voigt profile.

Most CARS thermometry studies use a broad-bandwidth Stokes beam that allows for the acquisition of an entire CARS spectrum with a single laser shot. The resolution of broad-bandwidth CARS spectra is usually limited to approximately 1 cm^{-1} by the combination of the spectrometer used to disperse the CARS signal beam and the CCD camera used to collect the dispersed spectra. Using the narrow-band dye laser in our study increases our resolution to 0.1 cm^{-1} , allowing us to determine line positions more accurately in the CARS spectra. This narrow-band Stokes laser, however, introduces the additional complication of requiring a simulation of its spectral line shape for use in fitting. Various empirical Stokes line shapes were tested by the examination of the goodness-of-fit of line shapes in high-temperature CARS spectra. To simulate accurately the experimental spectra required that both the N_2 and the O_2

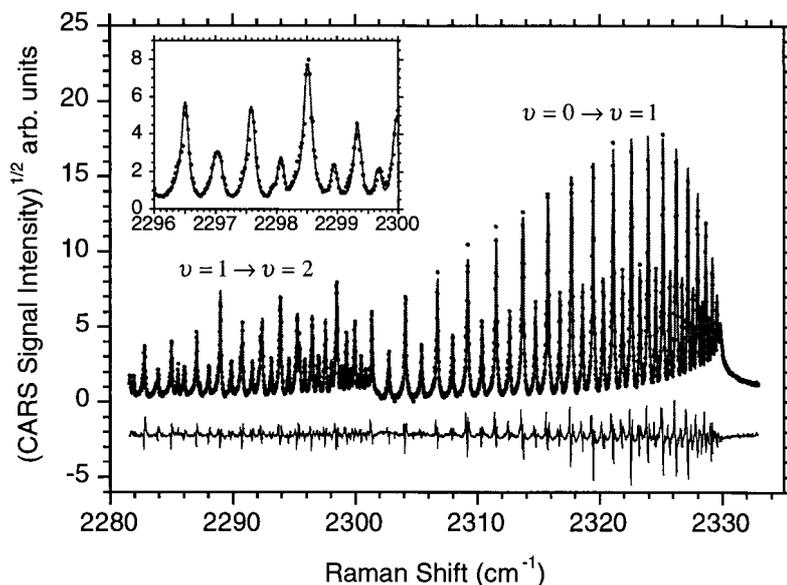


Fig. 2. CARS spectrum of N_2 at 1838 K. Data from both the fundamental and the first hot band were acquired and fitted. Each filled circle represents the average of 20 laser shots of data that were normalized by the laser pulse energies, and the curve represents the best spectral fit. The deviation between the fit and the data is displayed in the curve located below the spectrum.

CARS line shapes have a narrower peak at the line center and broader wings than a best-fit Voigt profile.

4. Comparison of N_2 and O_2 Coherent Anti-Stokes Raman Spectroscopy for Thermometry

We acquired N_2 and O_2 CARS spectra in room-temperature air and at various operating temperatures of the furnace. Figure 2 displays a N_2 CARS spectrum at 1838 K (determined from the fit). Both the actual CARS data (filled circles) and the best-fit spectrum (curve) are shown, and the deviation be-

tween the data and the fit is displayed by the curve that is located below the spectrum. We assumed that the composition was that of air: 79% N_2 and 21% O_2 . Both the fundamental band ($v = 0 \rightarrow v = 1$) and the first hot band ($v = 1 \rightarrow v = 2$) were included in the fit. Figure 2 includes an inset that displays the agreement between the fit and the data over a narrow frequency range. The excellent agreement seen from the inset illustrates the high accuracy with which the spectral constants have been determined because the prominent peaks result from

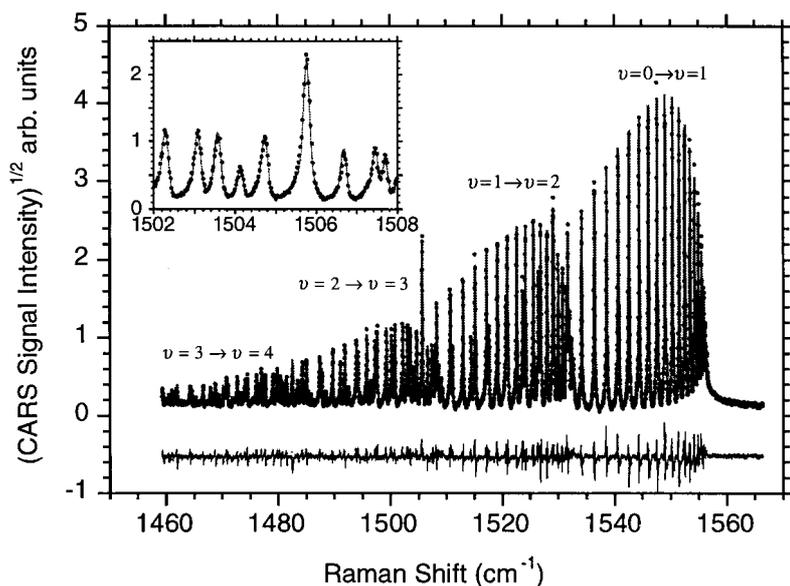


Fig. 3. CARS spectrum of O_2 at 1863 K. Data from both the fundamental and the first three hot bands were acquired and fitted. Each filled circle represents the average of 20 laser shots of data that were normalized by the laser pulse energies, and the curve represents the best spectral fit. The deviation between the fit and the data is displayed in the curve located below the spectrum.

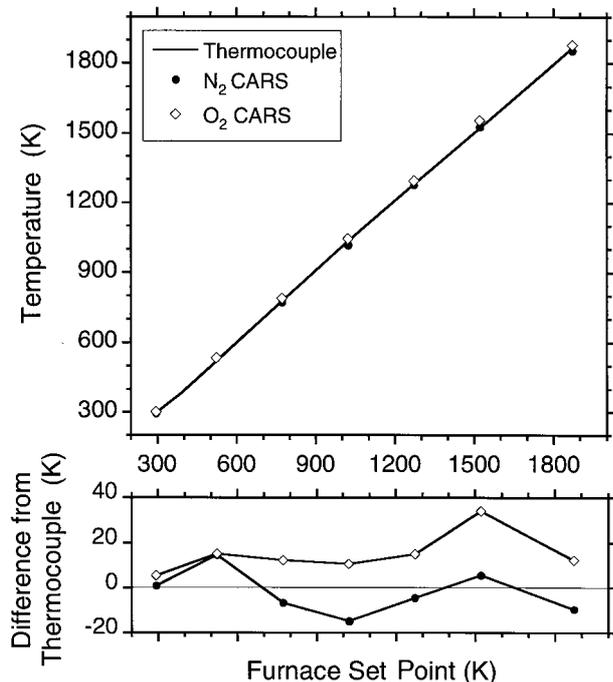


Fig. 4. Comparison between N₂ CARS temperature measurements, O₂ CARS temperature measurements, and thermocouple measurements in room-temperature air and in the furnace. Each symbol represents an average of three to seven temperatures acquired from different CARS spectra. The scatter in the temperature measurements is smaller than the size of the symbols in the upper plot.

overlaps between lines of the fundamental band and the first hot band. Constructive interference is responsible for the three large peaks seen at 2890.0, 2293.9, and 2298.5 cm⁻¹.

Figure 3 shows an O₂ CARS spectrum of the fun-

damental vibrational band ($v = 0 \rightarrow v = 1$) and the first ($v = 1 \rightarrow v = 2$), the second ($v = 2 \rightarrow v = 3$), and the third ($v = 3 \rightarrow v = 4$) hot bands at 1863 K (as determined from the fit). The spectral constants of Rouillé *et al.*¹⁹ provided accurate relative line positions for the fundamental band and the first two hot bands, but there was a slight deviation between the fit and the data for the third hot band. This deviation is expected because Rouillé *et al.*¹⁹ provided spectral constants that were calculated for the coupling of the rotational and the vibrational energy modes to only $v = 3$. The coefficients accurately predicted the constructive interference between the first and the second hot vibrational bands, as is apparent from the line at 1505.7 cm⁻¹. In general, we measured and analyzed data that encompassed only the fundamental band and the first two hot bands.

Figure 4 plots the N₂ and the O₂ CARS temperature measurements and the temperatures measured with the thermocouple against the furnace set-point temperature. Each plot symbol represents the average of three to seven CARS temperature measurements. The standard deviation of the measurements (<3%) is less than the size of the symbols in the upper plot. The maximum deviation between the N₂ CARS measurements and the thermocouple measurements is 3% at 520 K. There is similar agreement between the O₂ CARS measurements and the thermocouple readings. Including the first hot band in the temperature-fitting routine proved necessary: fitting only the fundamental band resulted in a 50-K underprediction of the temperature at 1880 K for O₂ CARS.

To assess O₂ CARS for thermometry at the higher temperatures found in O₂-enhanced combustion environments, we performed CARS measurements in a CH₄-O₂-N₂ flame produced with a Hencken burn-

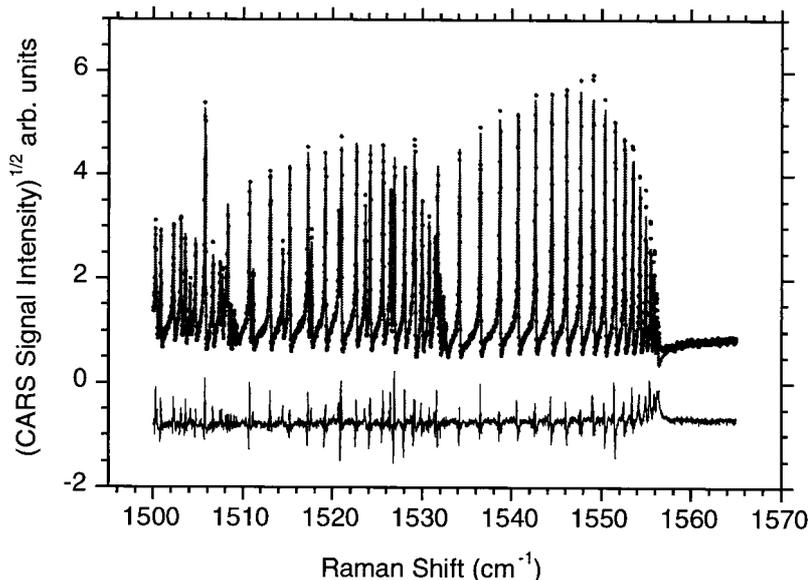


Fig. 5. CARS spectrum of O₂ at 2476 K. Data from both the fundamental and the first two hot bands were acquired and fitted. Each filled circle represents the average of 20 laser shots of data that were normalized by the laser pulse energies, and the curve represents the best spectral fit. The deviation between the fit and the data is displayed in the curve located below the spectrum.

er.²⁶ The rectangular burner was operated with flow rates of 11 slpm (standard liters per minute) CH₄, 52 slpm O₂, and 58 slpm N₂, as maintained by Tylan mass-flow controllers. The controllers were calibrated with a Matheson Model FM-1050 high-accuracy ($\pm 1\%$ full-scale) flow gauge. The N₂-O₂ mixture was flowed from the burner base, which was constructed of honeycomb stainless steel. Fuel was flowed separately from a matrix of small tubes imbedded in the 46 mm \times 22 mm honeycomb. Around the perimeter of the burner is a 12-mm-wide collar that was also constructed of honeycomb stainless steel and through which 25 slpm Ar was flowed to isolate the flame from the surrounding air. The burner produces a near-adiabatic flame because reactant mixing occurs near the burner surface and the flame is stabilized slightly above this premixed zone, reducing heat loss to the burner surface.

Figure 5 shows a typical O₂ CARS spectrum acquired in the flame. The temperature measured from several N₂ CARS spectra was 2469 ± 17 K, whereas the temperature measured by use of O₂ CARS was 2446 ± 42 K. Although they are in excellent agreement, these temperatures are, in fact, 300 K higher than the adiabatic-equilibrium temperature²⁷ that was calculated by use of the input gas-flow rates, which had an overall fuel-equivalence ratio of 0.42. We believe this discrepancy arises from a relatively higher output of the fuel tubes in the center (versus the edges) of the burner matrix. This effect, which was observed in previous studies, would have caused the fuel-air mixture to be closer to stoichiometric in the center. This outcome is in agreement with our fittings of the O₂ CARS spectra, which are consistent with an O₂ mole fraction of 13%, considerably lower than the adiabatic-equilibrium calculation of 24%.

6. Conclusions

CARS of O₂ has been shown to demonstrate a similar accuracy and precision to CARS of N₂ for thermometry from 294 to 2450 K. The spectral constants of Rouellé *et al.*¹⁹ predicted the O₂ relative line positions in the fundamental band and the first two hot bands. To test the utility of O₂ CARS in high-temperature oxygen-fuel environments, we acquired temperature measurements in a 2450-K flame by CARS of both N₂ and O₂. The measured temperatures agreed to within their approximately 3% scatter. O₂ CARS should thus be suitable for probing the temperature fields in fuel-lean O₂-enhanced or oxygen-fuel environments in which O₂ is present in sufficient quantities ($\approx 10\%$ or more). Lesser concentrations could also be probed with a potential loss of accuracy in the temperature measurement.

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